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International Classification:—B05. C07c. C08c, f, g. C10m.

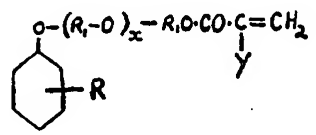
COMPLETE SPECIFICATION

Acrylates of Phenoxy Alcohol Ethers and Polymers thereof

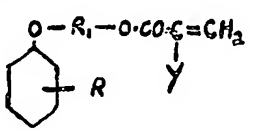
We, BRITISH RESIN PRODUCTS LIMITED, a British Company, of 21, St. James's Square, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to new polymerisable materials and the polymers and copolymers produced therefrom. In particular it relates to acrylic esters of alcohol ethers of phenols having aliphatic hydrocarbon substituents of 8—28 carbon atoms on their phenolic, aromatic nuclei.

Accordingly the present invention comprises the new polymerisable compounds having the formula



and polymers and copolymers derived therefrom. In the above formula R represents an aliphatic hydrocarbon radical of 8 to 28 and preferably at least 14 carbon atoms; each R_1 is a divalent hydrocarbon group of 2 to 8 carbon atoms; Y is either hydrogen or a methyl group; and x is an integer not greater than 5 and can be 0. When x is 0 the general formula becomes:



Particularly valuable compounds are obtained when R is a pentadecyl group attached in the 3-position with respect to the phenolic oxygen atom.

The monomeric compounds according to the present invention, either as such or when polymerised, find use as plasticisers for various resinous and polymeric substances. For example they may be employed as additives which act as plasticizers for rubbery materials such as natural rubber, reclaimed rubber and synthetic rubbers such as the normally solid copolymers of butadiene-1:3 and styrene, normally solid copolymers of butadiene-1:3 and acrylonitrile, normally solid homopolymers of butadiene-1:3, normally solid homopolymers of isoprene, normally solid homopolymers of isobutylene, normally solid homopolymers of chloroprene and mixtures thereof.

When employed as additives in this way the monomeric compounds of the present invention as well as their polymers impart greater stability towards heat ageing, greater elongation retention and reduction of increase in modulus to the material employed. In general, the ratio by weight of one or a combination of two or more of the compounds and/or their polymers to said materials is 0.5—40 parts of the former to 100 parts of the latter. Such combinations may have added thereto the other additives normally used in their compounding and the usual methods of curing can be employed. The compositions made in this way find application in the fields of electrical insulation, shower curtains, automobile tires and friction elements, such as brake linings and clutch facings.

A particular use of the monomeric compounds and their polymers is in combination with epoxy resins. Such combinations can be cured with any of the curing agents employed for curing epoxy resins to provide cured products which are softer, more pliable and more flexible than the products obtained in the

absence of the compounds according to the present invention. By epoxy resins is meant throughout this specification the glycidyl polyethers of aliphatic polyhydric alcohols or of polyhydric phenols, said polyethers having a 1,2-epoxy equivalency greater than 1 and being liquid at a temperature below 300°F. Such resins and the methods for making them are well known and examples may be found in the United States patent specifications 2,553,718 and 2,665,266. In general the ratio by weight of the monomeric compounds of the present invention and/or polymers thereof to one or a combination of two or more epoxy resins is in the range 2—75 parts, preferably 2—20 parts of the former to 100 parts of the latter.

Epoxy resin compositions containing the monomeric compounds of the present invention or their polymers may be used for coating paper, nylon, silk, asbestos, glass, cotton and Terylene (registered Trade Mark) which may be in the form of fibers, matting or woven fabric to provide good weatherproof and electrical insulating materials. They may also be used as casting resins in the electrical insulating field.

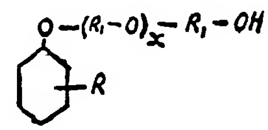
The monomeric materials of the present invention may be polymerised or copolymerised among themselves to give valuable polymers of various molecular weights. The polymerisation can be effected by the use of heat alone. If desired catalysts such as boron trifluoride and aluminium chloride may be employed to assist the polymerisation. The polymerisation may also be effected by using a peroxide catalyst with or without the aid of heat such as, for example, benzoyl peroxide, cumene peroxide and dicumyl peroxide.

The polymers derived from the monomeric compounds of the present invention are particularly useful as additives to improve the viscosity index of mineral motor oil lubricants. A small proportion of polymer is employed for the purpose and in general the ratio by weight of polymer to the motor oil is in the range 0.3—5 parts of polymer to 100 parts of oil.

The monomeric compounds find further use as intermediates in the production of further chemical compounds. They may be reacted with halogens, hydrogen halides such as hydrogen bromide or with hydrogen to produce corresponding compounds in which the double bond in the acrylic portion of the molecule has become saturated.

The monomeric compounds of the present invention can be prepared by the accepted methods of organic chemistry, starting from a phenol having an aliphatic hydrocarbon substituent of 8—28 carbon atoms attached to its phenolic, aromatic nucleus. An example of a suitable phenol is pentadecyl phenol, which may be produced by completely hydrogenating the unsaturated side chain of cardonal derived from cashew nut shell liquid, or gingkol. Other examples are the aliphatic phenols generally produced by reacting hydroxy benzene with certain chlorinated paraffins to produce the so-called " wax phenols " which are characterized as hydroxy benzene having an aliphatic hydrocarbon substituent on the nucleus with said substituent having a number of carbon atoms in the range of 14—28 carbon atoms.

To produce the compounds of the present invention the substituted phenol is most suitably converted to an alcoholic ether having the formula



in which the R groups and x have the same significance as hereinbefore stated. This conversion is most conveniently achieved by reacting the phenol with a cyclic ether, for example ethylene oxide, propylene oxide, butylene oxide and octylene oxide under etherification reaction conditions. A suitable process for this reaction is as follows:—

Catalytic amounts of an alkali, for example potassium hydroxide dissolved in methanol, are added to the substituted phenol and mass constantly stirred as its temperature is raised while being maintained under vacuum to remove the volatile solvents. Then at atmospheric pressure and elevated temperature the desired quantity of cyclic ether is introduced. After the required amount of oxide has reacted with the substituted phenol, the mass is cooled and neutralised and subsequently dehydrated under vacuum. Then the substantially completely dehydrated mass is filtered and the filtrate is recovered and consists essentially of an alcoholic ether having the above formula in which the value of x depends upon the amount of the cyclic ether which has reacted with the aliphatic phenol.

The alcoholic ethers produced above can be converted to the monomeric compounds of the present invention by various esterification techniques. For instance, they can be reacted with a suitable ester of acrylic or methacrylic acids to produce the desired products by trans-esterification. Alternatively compounds according to the present invention can be prepared by reacting a sodium salt of an alcoholic ether of the above formula with acrylyl or methacrylyl chloride, or by reacting an alcoholic ether directly with acrylic or methacrylic acid under esterification reaction conditions.

An alternative method of producing compounds according to the present invention comprises reacting two or more moles of a halogenated hydrocarbon, such as dibromo ethane with one mole of an alkali metal salt of a

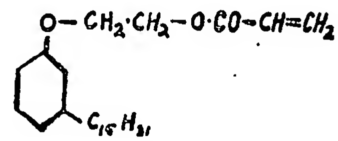
suitable aliphatic substituted phenol to yield the beta-bromo ethyl phenol ether. This ether is subsequently purified and reacted with a metal salt of acrylic or methacrylic acid to give the desired product.

The following examples illustrate the preparation of monomeric compounds according to the present invention and their polymerisation.

EXAMPLE 1.

A two liter, three neck flask equipped with stirrer, addition funnel and distillation set-up was loaded with 1200 grams (approx. 4 moles) of 3-pentadecyl phenol. This phenol was melted by raising the temperature thereof to approximately 60°C. and it was maintained at this temperature while 40 grams (0.22 mole) of potassium hydroxide in methanol (30% concentration) was added through the addition funnel. Then the mixture was topped in vacuo to 90°C. at 1 mm. of mercury pressure. Then under atmospheric conditions the resultant alkaline mixture was heated to 163°C. and held at this temperature while a stream of ethylene oxide was passed into the mixture through a large capillary tube. The addition of the ethylene oxide was continued under these conditions over a period of about 2¼ hours whereupon 194 grams (4.4 moles) thereof had become absorbed or reacted with the alkaline mixture. Then the mass was cooled to about 100°C. and neutralised with 15 grams of concentrated hydrochloric acid in 15 grams of water. The neutral mass was dehydrated at a temperature of 100°C. and 25 mm. of mercury pressure, and then filtered at 100—110°C. through a Buchner funnel, the filtrate being recovered, the filtrate was then distilled at 1.5 mm. of mercury pressure in a two liter flask equipped with a distillation column filled with metal helices. A yield of 1209 grams of substantially pure β-hydroxy-(3-pentadecyl phenoxy) ethane was collected between 222—234°C. in four fractions which had identical melting points of 48.5 to 49.5°C. The percentage of free 3-pentadecyl phenol was less than 0.1%.

Into a three neck flask fitted with a Vigreux Column were charged 402 grams of the above β-hydroxy-(3-pentadecyl phenoxy) ethane, 344 grams of methyl acrylate, 10 grams of hydroquinone as polymerisation inhibitor and 5 grams of para toluene sulphonic acid. The mixture while being constantly stirred was externally heated to a temperature such that it boiled and the azeotropic mixture in the column was at a temperature of 62—65°C. and contained approximately 55% of methanol. After being maintained for approximately 14 hours under these conditions 242 cc of azeotrope containing 37 grams of methanol was collected. The excess methyl acrylate was removed from the reaction mass in the flask at 30 mm. of mercury pressure to a pot temperature of 121°C. The para-toluene sulphonic acid catalyst was neutralised with 2.67 grams of sodium bicarbonate in 20 grams of water and the mixture dehydrated to 80°C. at 30 mm. of mercury pressure. A 20 gram sample of the dehydrated, neutralised mass was dissolved in 20 grams of heptane and this solution was twice washed with 40 cc. of a 2% aqueous solution of sodium hydroxide. The heptane layer was acidified with acetic acid and dried with anhydrous magnesium sulfate. The magnesium sulphate was filtered and the heptane stripped from the filtrate. The resultant product was distilled at 2×10^{-3} mm. of mercury pressure, pot temperature 240—245°C. and column temperature of 178—182°C. By repeating this process on the rest of the material an overall yield of 295 grams of distillate having a melting point of 33.5—35.5°C. was obtained. Quantitative hydrogenation and saponification equivalent indicated 90% pure acrylate. This product consisted essentially of a compound of the following formula:

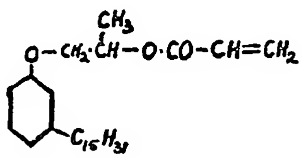


EXAMPLE 2.

A one litre three neck flask equipped with stirrer, addition funnel and distillation set-up was loaded with 304 grams of 3-pentadecyl phenol (1.0 mole). The flask was heated to 80°C. and 3.0 grams of 50% aqueous sodium hydroxide added to the molten mass. Upon heating to 110°C. at 15 mm. of mercury pressure all the water distilled off. A 200 cc. flask containing 76.8 grams (1.32 moles) of cold propylene oxide was gently warmed in a water bath at 45—50°C. and the resultant gaseous propylene oxide passed in for two hours through a capillary below the surface of the molten phenol, which was kept at a temperature of 163°C. An increase in weight of 62.0 g. indicated that 1.07 moles of propylene oxide had been absorbed. Quantitative test indicated less than 0.1% free phenol. The reaction product was neutralised with 7.6 grams of 18 per cent hydrochloric acid, and the water removed by distillation at 15 millimetres of mercury presure and 110°C. pot temperature. After adding 5 grams of filter aid the hot product was filtered and the filtrate distilled at 0.5 millimetres pressure at 206—214°C. The melting point was 38—41.0°C. and the yield was 296 grams of α-(3-pentadecyl phenoxy)-β-hydroxy propane.

To a three necked flask fitted with a wire gauze packed column was added 290 grams (0.8 moles) of the alpha-(3-pentadecyl phenoxy) beta hydroxy propane, described above, 320 grams (3.2 moles) of ethyl acrylate, 8

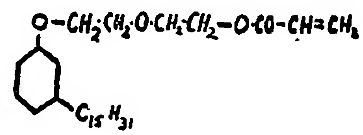
grams of hydroquinone, and 6 grams of para-toluene sulphonic acid. The ethyl alcohol/ether acrylate azeotrope distilled at 68.83°C. at a rate of one drop in 5 seconds over a period of 16 hours. The reaction product was stripped of excess ethyl acrylate to a pot temperature of 120°C. at 2 millimeters of mercury presure and weighed 372 grams. After dissolving the crude material in 350 grams of diethyl ether the product was washed with 600 milliliters of 1:1 mixture of 5 per cent sodium carbonate and methanol. After separating the hydrophobic layer containing the product it was washed with 500 milliliters of 1:1 methanol-water and twice with 300 milliliter portions of 25 per cent sodium chloride solution. After drying with anhydrous magnesium sulfate the ether solution of the acrylate product was filtered, stripped of solvent to yield a crude product weighing 323 g. The product was distilled in a liter flask equipped with a vigreux column and using a mercury diffusion pump to produce a vacuum of 36×10^{-3} millimeters of mercury. A middle fraction of 200 grams of light amber liquid was collected at 176—186°C. at a rate of 1.3 drops per second. Hydrogenation indicated a purity of 98.8%. The formula of this product is:



Example 3.

A two liter three neck flask equipped with stirrer, still set up and dropping funnel was loaded with 1216 grams of molten 3-pentadecyl phenol and 24 grams of 50 per cent aqueous sodium hydroxide added with stirring. The mass was dehydrated at 40 millimeters pressure to a pot temperature of 120°C. After heating the melt to 155°C. ethylene oxide was passed in through a capillary over a period of three and a half hours, resulting in an absorption of 352 grams of oxide. After cooling to 80°C. the mass was neutralised with 62.4 grams of 18 per cent hydrochloric acid and the water removed by distillation at a pressure of 40 millimeters of mercury to a pot temperature of 120°C. After adding 15 grams of filter aid the product was filtered hot through a Buchner funnel to yield 1525 grams of pale amber solid. A preliminary vacuum distillation through a Vigreux column of 1400 grams of product yielded 471 grams of liquid boiling at 225—238°C. at 0.5 millimeters of mercury pressure. Upon redistillation of this liquid through a further distillation column 155.5 grams of a pure white solid, melting at 36—38°C., was collected at 222—224°C. and 0.4 millimeters of mercury pressure. The product was β-hydroxy β-(3-pentadecyl phenoxy)-diethyl ether.

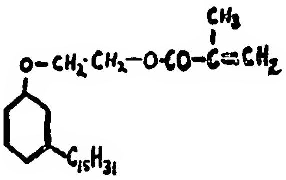
Into a 500 milliliter three neck flask equipped with a 30 centimeter glass helix packed column, stirrer and nitrogen inlet tube was loaded 57 grams (0.143 moles) of the above β-hydroxy β¹-(3-pentadecyl phenoxy) diethylether, 65 grams (0.65 moles) of ethyl acrylate, 1.5 grams of hydroquinone and 1.0 grams of para-toluenesulphonic acid. After heating for six hours to maintain a boiling temperature of 68—83°C. 42 grams of azeotrope containing 6.7 grams of ethanol, as determined by water washing was distilled from the reaction mixture. The residue was dissolved in 150 grams of diethylether and washed free of hydroquinone, acid, and salts by using two 75 milliliter portions of 25% sodium chloride solution containing 2% sodium hydroxide. A third wash with saturated sodium chloride left the product solution neutral. The soluton was dried over 100 grams of anhydrous magnesium sulfate, filtered the next day and the diethyl ether stripped from the product under vacuum. The product weighed 52.5 grams. Quantitative hydrogenation indicated 83 per cent conversion to the ester, β-acrylate-β¹-(3-pentadecyl phenoxy) diethyl ether of the following formula:



Example 4.

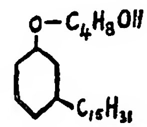
A two liter, three neck flask equipped with stirrer, 30 centimeter glass helix packed column and a nitrogen inlet tube was loaded with 304 grams (0.85 moles) of β-hydroxy-(3-pentadecyl phenoxy)-ethane, as prepared in Example 1, 400 grams (4.0 moles) of methyl methacrylate, 8 grams of hydroquinone, and 6 grams of para toluenesulphonic acid. The reaction mass was heated to maintain a distillation temperature of the azeotrope of 62—68°C. over a period of 8 hours. The azeotrope collected weighed 147 grams and contained 27 grams of methanol. The remaining methyl methacrylate was stripped in vacuum and combined with that recovered in the azeotrope to equal a recovery of 307 grams. The residual reaction product was dissolved in 370 grams of diethyl ether and washed with two 300 milliliter portions of 10 per cent sodium carbonate containing 20 per cent sodium chloride followed by two 250 milliliter washes with 10 per cent sodium chloride. The ether layer was then dried with 200 grams of anhydrous sodium sulfate by standing 24 hours and then filtering. The ether was stripped in vacuo and the residual product distilled at 4.4×10^{-3} mm. pressure of mercury. A fraction weighing

160 grams was cut boiling at 175—183°C. Quantitative hydrogenation of the pale amber liquid product indicated that it was practically 100% pure β-methacrylate-(3-pentadecyl-phenoxy)-ethane of the following formula:

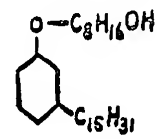


Other alcoholic ethers, from which mono-meric compounds according to the present invention can be prepared, are themselves prepared as follows:

Into a two liter, three necked flask set up as in Example 1 was introduced 608 grams of molten 3-pentadecyl phenol (2 moles) and 6.0 grams of 50 per cent aqueous sodium hydroxide. The water was removed by distillation at 15 millimeters of mercury pressure to a pot temperature of 110°C. The melt was heated to 163°C. and 196 grams (2.72 moles) of mixed 1, 2 and 2, 3 butylene oxide isomers were added through the dropping funnel which had its tip below the surface of the molten 3-pentadecyl phenol. After 5½ hours the reaction was substantially complete since a quantitative test indicated only 1.1 per cent 3-pentadecyl phenol remaining in the mixture. The product was neutralised with 20 grams of 18 per cent hydrochloric acid, dehydrated to a pot temperature of 110°C. at a pressure of 2—3 millimeters of mercury, 10 grams of filter aid added and filtered hot. A yield of 743 grams of an alcoholic ether having the following formula was obtained:



A one liter flask equipped as in Example 1 was loaded with 304 grams (one mole) of 3-pentadecyl phenol and 4.5 grams of 50 per cent aqueous sodium hydroxide added. The molten mass was dehydrated to a pot temperature of 110°C. at a presure of 15 millimeters of mercury. The temperature was raised to 171°C. and 85 per cent mixed 1:2 and 2:3-isomers of octylene oxide added through a dropping funnel whose tip went below the surface of the molten 3-pentadecyl phenol. The addition was complete in three hours. After five hours more of additional heating at 171°C. the reaction product contained 93 per cent ether. The cooled product was neutralised with 14.4 grams of 18 per cent hydrochloric acid and unreacted ocetylene oxide and water removed at 1 to 2 millimeters of mercury pressure and a pot temperature of 120°C. After addition of 10 grams of filter aid the product was filtered to yield 433 grams of a reaction product which was a mixture of isomers of the following empirical formula



The polymerisation of monomeric compounds according to the present invention is illustrated in the following examples:

EXAMPLE 5.

beta-acrylate (3-pentadecyl phenoxy) ethane undistilled Product of Example 1	12.5 grams
Heptane, pure dry	12.5 grams
Benzoyl Peroxide	0.125 grams

The three materials were weighed into a 25 x 15 centimeter Pyrex test tube with a 10 millimeter tube attached at one end. (Pyrex is a registered Trade Mark). The benzoyl peroxide was dissolved in the liquids at 60°C. and then the tube was immersed in powdered dry ice which froze the liquids. After evacuating the tube to one millimeter of mercury pressure the 10 millimeter tube was constricted and sealed off with a gas-oxygen torch. Upon cooling of the seal the tube was wrapped in paper and placed upright in an oven at 60°C. for 185 hours. After cooling to room temperature the tube was opened and the contents stripped of solvent in vacuo. The viscous semi-solid upon quantitative hydrogenation was almost completely saturated indicating complete homo-polymerisation of the beta acrylate (3-pentadecyl phenoxy ethane).

EXAMPLE 6.

Same procedure as in Example 5 was followed except the product of Example 1 was replaced by the product of Example 2. Conversion was 89 per cent. The unreacted monomer was removed by hot methanolic wash followed by molecular distillation at 205°C. and a pressure of 0.18 mms. of mercury. The product, poly-[alpha-acrylato beta-(3-pentadecyl phenoxy) propane], was a thick, viscous semi-solid.

EXAMPLE 7.

The same quantities and procedure as in

Example 5 were used except that the product of Example 1 was replaced by the product of Example 3. The polymerisation was complete as indicated by no hydrogen uptake on quantitative hydrogenation with 5 per cent palladium on carbon catalyst in dioxane solution. The polymer, poly-[beta-acrylato-β^1-(3-penadecyl phenoxy) diethyl ether], was a thick liquid.

EXAMPLE 8.

The same procedure as in Example 6 was used except that the product of Example 2 was replaced by the product of Example 4. The polymerisation was complete as indicated by the hydrogenation test. The polymer, poly-[beta-methacrylato alpha-(3-pentadecyl phenoxy)-ethane], was a solid.

The polymers of Examples 5 to 8, were used as viscosity index improvers. The American Society for Testing Materials method of determining the viscosity index was followed by using a Saybolt Universal Viscosimeter. An additive free SAE 10 mineral motor oil having a viscosity index of 89.8 was used. The polymers were dissolved in 2 per cent concentration in the oil and Saybolt Viscosity in seconds taken at 100°F. and 210°F. The ASTM tables were used to calculate viscosity index.

Additive	Viscosity Index
None	89.8
Polymer of example 5	119.5
" " " 6	114.5
" " " 7	122.0
" " " 8	124.0

The viscosity index improvement was significant for each polymer used.

The monomeric compounds of the present invention and their polymers can be used to improve the properties of epoxy resins as illustrated in the following examples.

EXAMPLE 9.

The following mixtures X and Y were made up for the purpose of comparison, with the former being the control, and the epoxy resin used in each case was a "bis-phenol A"-epichlorhydrin condensate having an epoxide equivalent of 190—210 grams (2,2 di (para-hydroxy phenyl) propane-epichlorhydrin condensate).

Mix X	Grams
Epoxy resin	10
triethylenetetramine	1

Mix Y	Grams
Epoxy resin	10
triethylenetetramine	1
Product of Example 2	2

The mixtures X and Y were respectively poured into aluminium weighing dishes and each subsequently cured for 2 hours at 25°C. and then for 16 hours at 120°C. At the end of the 16-hour period, both mixtures were found to be cured to the solid state. There was no indication of any incompatibility in the cured mix Y. The cured resins were tested for hardness and it was found that cured X had a Barcol 935 hardness of 84 and cured Y had a Barcol 935 hardness of 76, and that the latter was more flexible than the former.

EXAMPLE 10.

The following mixtures R and S were made up for the purpose of comparison, with the former being in control. An epoxy resin used in each case was:

3-pentadecadienyl phenol (cardanol) reacted with phenol to form a bisphenol and this condensate was reacted with epichlorhydrin in the presence of sodium hydroxide, employing the general procedure set forth in U.S. patent 2,665,266, to provide a glycidyl polyether of the bisphenol as a viscous liquid having an epoxide equivalent of 450—550.

Mix R	Grams
Epoxy resin	10
triethylenetetramine	0.8

Mix S	Grams
Epoxy resin	10
triethylenetetramine	0.8
Product of example 2	2

The mixtures R and S were respectively poured into aluminium weighing dishes and each subsequently cured for two hours at 25°C. and then for sixteen hours at 120°C. At the end of the 16-hour period, both mixtures were found to be cured to the solid state. There was no indication of any incompatibility in the cured mix S. The cured resins were tested for hardness and it was found that cured R had a Shore Durometer D hardness of 75 and cured S had a Shore Durometer D hardness of 35. The cured S was was found to be softer, more pliable and more flexible than cured R.

The following example illustrates the advantageous results obtained by adding the monomeric compounds of the present invention to butadiene/styrene synthetic rubber composition, all the proportions being by weight.

EXAMPLE 11.

Synthetic rubber composition:

GRS—1500 (butadiene/styrene rubber)	100.0
Carbon black	75.0
Fast curing ZnO	3.0
Stearic Acid	1.0
Diphenyl amine-acetone reaction product as antioxidant	1.0
n-Cyclohexyl 2-benzothiazole sulfenamide	1.2
Sulphur	1.1
Plasticizer	variable as shown below

Product of Example 1	0	10	20	30	0
Dioctyl Sebacate	0	0	0	0	30
Original Properties					
Modulus at 200% psi.	1493	1090	611	375	432
Tensile Strength psi.	3260	2960	1980	1311	1840
Elongation %	338	388	438	450	412
Shore A durometer	71	66	56	51	53
Aged Properties 70 hrs. at 70°C.					
Modulus at 200% psi.	2420	1520	988	552	744
Tensile Strength psi.	2960	2910	2390	1610	1790
Elongation %	225	300	350	388	338
Shore A Durometer	81	74	66	59	62

In the above the curing of the composition was affected at 142° C. for 1 hour.

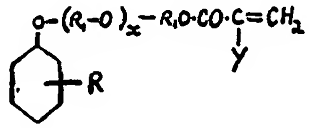
The monomeric compounds of the present invention as well as their homopolymers may be employed as coating compositions on a base. They may be dissolved in suitable solvents with or without a polymerizing agent, depending upon whether a monomer or polymer is used and thereafter heated in the presence of a drier to drive off the solvent and convert the monomers or polymers to the substantially solid state. The polymers can be combined with any of the well-known metallic-salt drying agents, for example those employed in linseed oil paints, and that such combinations are capable of being air-dried at elevated temperatures. Consequently such combinations find utility as airdrying surface protectors as illustrated in example 12.

EXAMPLE 12

Five grams of the product of example 2 were dissolved in five parts of xylene and to this solution was added .05 grams of cobalt naphthenate (6% cobalt) as drying agent. The mix was stirred to uniformity and then brushed on to a clean piece of tin plate. The formed film was allowed to stand in a room at 70°F. while the xylene evaporated. Then the coated plate was subjected to a temperature of 180°C. for four hours and allowed to stand in a room at 70°F. overnight. The next morning the coated plate was examined and the film on the plate was found to be tack-free, had good adherence to the plate and was tough and flexible.

WHAT WE CLAIM IS:—

1. A polymerisable compound having the formula

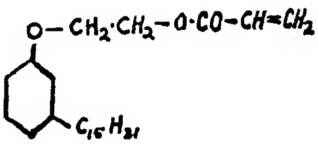


in which R represents an aliphatic hydrocarbon radical of 8 to 28 carbon atoms, each R_1 is a divalent hydrocarbon group of 2 to 8 carbon atoms, Y is either hydrogen or a methyl group and x is an integer, including 0, not greater than 5.

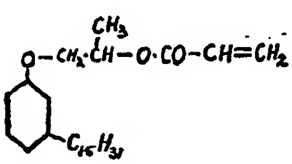
2. A compound as claimed in claim 1, wherein the aliphatic hydrocarbon radical R contains at least 14 carbon atoms.

3. A compound as claimed in claim 1, wherein the aliphatic hydrocarbon radical R is a pentadecyl group attached in the 3-position with respect to the phenolic oxygen atom.

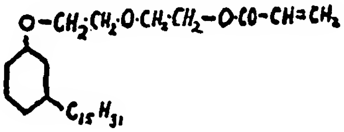
4. A polymerisable compound having the formula



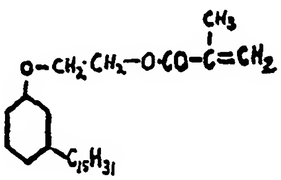
5. A polymerisable compound having the formula



6. A polymerisable compound having the formula



7. A polymerisable compound having the formula



8. Polymers obtained by the polymerisation or copolymerisation among themselves of polymerisable compounds as claimed in any of the preceding claims.

9. A lubricant comprising a mineral motor oil and a small proportion of a polymer as claimed in claim 8 to increase the viscosity index of the oil.

10. A composition comprising an epoxy resin, as hereinbefore defined, and a monomeric compound or compounds as claimed in any of the preceding claims 1 to 7 or a polymer as claimed in claim 8, said monomeric material or said polymer being present in an amount by weight of 2 to 75 parts thereof to every 100 parts of epoxy resin.

11. Plasticised compositions comprising natural rubber, reclaimed rubber, normally solid copolymers of butadene-1:3 and styrene, normally solid copolymers of butadiene-1:3 and acrylonitrile, normally solid homopolymers of butadiene-1:3, normaly solid homopolymers of isoprene, normally solid homopolymers of isobutylene, or normally solid homopolymers of chloroprene and a plasticising amount of a monomeric compound or compounds as claimed in any of the preceding claims 1 to 7 or of a polymer as claimed in claim 8.

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